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(54) **Process for the preparation of a catalyst component for the polymerisation of an olefin**

(57) The invention is directed to a process for the preparation of a catalyst component for the polymerisation of an olefin by:

a) contacting metallic magnesium with an organic halide RX, where R is an organic group containing from 1 to 20 carbon atoms and X is a halide, whereupon the dissolved reaction product I is separated from the solid residual products and whereafter,
b) an alkoxy group or aryloxy group-containing silane compound is added to the obtained reaction product I, whereupon the precipitate formed is purified to obtain reaction product II,
c) which subsequently is contacted with $TiCl_4$ as halogenized titanium compound and is purified to obtain a catalyst component, wherein,

in step b the silane compound and reaction product I are introduced simultaneously to a device.

Description

[0001] The invention is directed to a process for the preparation of a catalyst component for the polymerisation of an olefin.

[0002] Catalyst components on a support for the preparation of polyolefins have a high activity and a high stereospecificity. These catalyst components are already known for a long time. Essential elements for the preparation of such catalyst components are a magnesium-containing support and a titanium compound attached thereto. For the polymerisation of olefins also an alkylaluminum compound is needed as a cocatalyst.

[0003] High activity supported catalyst components are the most frequently used catalyst components for the polymerisation of olefins, such as for instance propylene. By the high activity of the catalyst component a high yield of the polyolefin is obtained per weight percentage of the titanium compound in the catalyst component. Therefore it is no longer needed to remove the catalyst component from the polyolefin produced.

[0004] There are several methods to prepare the magnesium-containing support of the catalyst component. It is for instance possible to grind the magnesium-containing support, spraydrying it or to precipitate the magnesium-containing support. The magnesium-containing support can further be treated with a halogenating compound to prepare the magnesium-containing support. Several other methods to prepare magnesium-containing supports are for instance described by E.P. Moore (Jr.), Polypropylene Handbook, Hansen Publishers, 1996, p. 22.

[0005] A process for the preparation of such a supported catalyst component is for instance described in WO-A-96/32427.

[0006] In this patent application a process for the preparation of a catalyst component for the polymerisation of an olefin is described. In the preparation of the catalyst component a magnesium compound is contacted with a titanium compound wherein the magnesium compound is obtained by:

a) contacting metallic magnesium with an aromatic halide RX, where R is an aromatic group containing from 6 to 20 carbon atoms and X is a halide, whereupon the dissolved reaction product I is separated from the solid residual products and whereafter,
b) an alkoxy group or aryloxy group-containing silane compound is added to the obtained reaction product I at a temperature of from -20 to 20°C, whereupon the precipitate formed is purified to obtain reaction product II,

- which subsequently, during a step c, is contacted with $TiCl_4$ as halogenized titanium compound and the resulting product is purified to obtain a catalyst component.

[0007] Although the performance of this catalyst component is very good and this catalyst component already shows a high activity and selectivity, a more improved catalyst component is obtained by the process of the present invention wherein in step b the silane compound and reaction product I are introduced simultaneously to a device.

[0008] Here and hereafter "simultaneous introduction" means the introduction of reaction product I and the silane compound in such a way that the Mg/Si ratio does not substantially vary during introduction of these compounds to the device.

[0009] This process has the advantage that the morphology of the catalyst particles improves; especially for the larger catalyst particles. Here and hereafter 'morphology' does not only refer to the shape of the catalyst particles, but also to the particle size distribution and the bulk density of the catalyst particles.

[0010] The polyolefin powder produced by using the catalyst component has the same morphology as the catalyst component; this is a known effect and is called the "replica effect" (S. van der Ven, Polypropylene and other Polyolefins, Elsevier 1990, p. 8-10). Using the catalyst compound prepared according to the process of the invention almost round polymer particles are obtained with a length/diameter ratio (1/d) smaller than 2 and a good powder flowability, while according to WO-A-96/32427 elongated polymer particles are obtained with a 1/d of more than 2.5.

[0011] During step b the dissolved reaction product I, obtained after carrying out step a, is brought into contact with an alkoxy group or aryloxy group-containing silane compound in such a way that reaction product I and the silane compound are introduced simultaneously to a device.

[0012] The device can have various forms; the device can be a device in which the silane compound is premixed with reaction product I, but the device can also be the reactor wherein reaction product II is formed.

[0013] The device for premixing the silane compound and reaction product I can be a device in which the premixing takes place in a dynamic or a static way. Premixing in a dynamic way takes place by, for instance, mixing, stirring, shaking and by the use of ultrasonic waves. Premixing in a static way takes place in, for instance, a static mixer or in a tube wherein the silane compound and reaction product I are contacted. For the preparation of the catalyst component in big amounts both static and dynamic mixing can be used. Premixing in a dynamic way is preferably used when the catalyst component is prepared in small amounts. For the preparation of the catalyst component in big amounts preferably a static mixer is used for premixing the silane compound and reaction product I. Preferably, the silane compound

and reaction product I are premixed before the mixture is introduced to the reactor wherein reaction product II is formed. In this way the catalyst component formed gives polymer particles with the best morphology.

[0014] Premixing is performed during 0.1 to 300 seconds; preferably during 1 to 50 seconds.
The temperature during premixing is 0 to 80 °C; preferably 10 to 50 °C.

[0015] The silane compound and reaction product I can be continuously or batch-wise introduced to the device. Preferably, the silane compound and reaction product I are introduced continuously to the device.

[0016] The formation of reaction product II normally takes place at a temperature between -20 and 100 °C; preferably at a temperature of from 0 to 80 °C.

[0017] Preferably, reaction product I is contacted with the alkoxy group or aryloxy group-containing silane compound in the presence of an inert hydrocarbon solvent such as the solvents mentioned further as dispersant in the discussion of step a. The solvent can be a solvent for the silane compound, a dispersant for reaction product I or be present in the reactor wherein reaction product II is collected. Combinations of these three possiblities are also possible.

[0018] Preferably, the reactor wherein reaction product II is collected, is a stirred reactor.

[0019] The Si/Mg molar ratio during step b may vary from 0.2 to 20. Preferably, the Si/Mg molar ratio is from 0.4 to 1.0.

[0020] The product from step b, reaction product II, is usually rinsed with an inert hydrocarbon solvent and then used for the further preparation of the catalyst component in step c.

[0021] The following examples of alkoxy group or aryloxy group-containing silane compounds may be mentioned: tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, tetraisobutoxysilane, tetraphenoxysilane, tetra (p-methylphenoxy) silane, tetrabenzyloxysilane, methyltrimethoxysilane, methyltriethoxysilane, methyltributoxysilane, methyltriphenoxysilane, methyltriphenoxysilane, ethyltriethoxysilane, ethyltriisobutoxysilane, ethyltriphenoxysilane, butyltrimethoxysilane, butyltriethoxysilane, butyltributoxysilane, butyltriphenoxysilane, isobutyltriisobutoxysilane, vinyl triethyoxysilane, allyltrimethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, benzyltriphenoxysilane, methyltriallyloxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, dimethyldiisopropyloxysilane, dimethyldibutoxysilane, dimethyldihexyloxysilane, dimethyldiphenoxysilane, diethyldiethoxysilane, diethyldiisobutoxysilane, diethyldiphenoxysilane, dibutyldiisopropyloxysilane, dibutyldibutoxysilane, dibutyldiphenoxysilane, diisobutyldiethoxysilane, diisobutyldiisobutoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, diphenyldibutoxysilane, dibenzyldiethoxysilane, divinyl diphenoxysilane, diallyldipropoxysilane, diphenyldiallyloxysilane and methylphenyldimethoxysilane.

[0022] Preferably use is made of tetraethoxysilane.

[0023] Step a in the process for the preparation of the catalyst component of the invention is carried out by contacting metallic magnesium with an organic halide RX.

[0024] All forms of metallic magnesium may be used, but preferably use is made of finely divided metallic magnesium, for example magnesium powder. To obtain a fast reaction it is preferable to heat the magnesium under nitrogen prior to use. In the organic halide RX, R is an organic group preferably containing from 1 to 20 carbon atoms and X preferably is chlorine or bromine.

[0025] Examples of the organic group R are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, hexyl, octyl, phenyl, tolyl, xylyl, mesityl and benzyl. Combinations of two or more organic halides RX can also be used.

[0026] The magnesium and the organic halide RX can be reacted with each other without the use of a seperate dispersant; the organic halide RX is then used in excess. The organic halide RX and the magnesium can also be brought into contact with one another in the presence of an inert dispersant. Examples of dispersants are: aliphatic, alicyclic or aromatic dispersants containing 4-20 carbon atoms.

[0027] Preferably, in step a an ether is added to the reaction mixture. Examples of ethers are: diethyl ether, diisopropyl ether, dibutyl ether, diisobutyl ether, diisoamyl ether, diallyl ether, tetrahydrofuran (THF) and anisole. It is preferred for dibutyl ether and/or diisoamyl ether to be used.

[0028] Preferably, an excess of chlorobenzene is used as the organic halide RX. Thus, the chlorobenzene serves as dispersant as well as organic halide RX. The organic halide/ether ratio acts upon the activity of the catalyst component. The chlorobenzene/dibutyl ether volume ratio may for example vary between 75:25 and 35:65.

[0029] When the chlorobenzene/dibutyl ether ratio decreases, the bulk density of the polyolefine powder prepared with the aid of the catalyst component becomes lower and when the chlorobenzene/dibutyl ether ratio increases, the amount of the dissolved reaction product I becomes lower. Consequently, the best results are obtained when the chlorobenzene/dibutyl ether volume ratio is between 70:30 and 50:50.

[0030] Small amounts of iodine and/or alkyl halides can be added to cause the reaction between the metallic magnesium and the organic halide RX to proceed at a higher rate. Examples of alkyl halides are butyl chloride, butyl bromide and 1,2-dibromoethane. When the organic halide RX is an alkyl halide iodine and 1,2-dibromoethane are preferably used.

[0031] The reaction temperature for step a normally is between 20 and 150°C; the reaction time between 0.5 and 20 hours.

[0032] After the reaction is completed, the dissolved reaction product I is separated from the solid residual products.

[0033] The further preparation of the catalyst component is carried out by contacting, during a step c, the purified

reaction product II with $TiCl_4$.

[0034] Preferably an internal electron donor is also present during step c. Also mixtures of internal electron donors can be used. Examples of internal electron donors are carboxylic acids, carboxylic anhydrides, esters of carboxylic acids, halide carboxylic acids, ethers, ketones, amines, amides, nitriles, aldehydes, alcoholates, sulphonamides, thioethers, thioesters and organic compounds containing a heteroatom, such as nitrogen, oxygen and phosphorus.

[0035] Examples of carboxylic acids are formic acid, acetic acid, propionic acid, butyric acid, isobutanoic acid, acrylic acid, methacrylic acid, maleic acid, fumaric acid, tartaric acid, cyclohexanoic monocarboxylic acid, cis-1,2-cyclohexanoic dicarboxylic acid, phenylcarboxylic acid, toluenecarboxylic acid, naphthalene carboxylic acid, phthalic acid, isophthalic acid, terephthalic acid and trimellitic acid. Anhydrides of the aforementioned carboxylic acids can be mentioned as examples of carboxylic anhydrides, such as acetic acid anhydride, butyric acid anhydride and methacrylic acid anhydride.

[0036] Examples of esters of carboxylic acids that can be mentioned are butyl formate, ethyl acetate, butyl acetate, ethyl acrylate, methyl methacrylate, isobutyl methacrylate, methylbenzoate, ethylbenzoate, methyl-p-toluate, ethyl-α-naphthoate, monomethyl phthalate, dibutyl phthalate, diisobutyl phthalate, diallyl phthalate and diphenyl phthalate.

[0037] Examples of halide carboxylic acids that can be mentioned are the halides of the above carboxylic acids, such as acetyl chloride, acetyl bromide, propionyl chloride, butanoyl chloride, butanoyl iodide, benzoyl bromide, p-toluyl chloride and phthaloyl dichloride.

[0038] Examples of suitable ethers are diethyl ether, dibutyl ether, diisoamyl ether, anisole and ethylphenyl ether, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2-ethyl-2-butyl-1,3-dimethoxypropane 2-isopropyl-2-isopentyl-1,3-dimethoxypropane and 9,9-bis(methoxymethyl)fluorene. Also, tri-ethers can be used.

[0039] Examples of organic compounds containing a heteroatom are thiophenol, 2-methylthiophene, isopropyl mercaptan, diethylthioether, diphenylthioether, tetrahydrofuran, dioxane, dimethylether, diethylether, anisole, acetone, triphenylphosphine, triphenylphosphite, diethylphosphate and diphenylphosphate.

[0040] Preferably dibutyl phthalate is used as the internal electron donor.

[0041] The $TiCl_4$/Mg molar ratio during step c preferably is between 10 and 100. Most preferably, this ratio is between 10 and 50. The molar ratio of the electron donor, if used, relative to the magnesium in step c may vary between 0.05 and 0.75. Preferably this molar ratio is between 0.1 and 0.4.

[0042] During step c use is preferably made of a solvent of an aliphatic or aromatic hydrocarbon compound. Most preferably, the solvent is toluene or chlorobenzene.

[0043] The reaction temperature during step c is preferably between 50-150°C, most preferably between 60-120°C. At higher or lower temperatures the activity of the catalyst component prepared according to the process of the invention becomes lower. The obtained reaction product is purified to obtain a catalyst component.

[0044] The catalyst component of the invention is suitable for the preparation of polyolefines by polymerising an olefine in the presence of the catalyst component and a cocatalyst. The cocatalyst generally is an organometallic compound containing a metal from group 1, 2, 12 or 13 of the Periodic System of the Elements (Handbook of Chemistry and Physics, 70th Edition, CRC Press, 1989-1990). Preferably the cocatalyst is an organoaluminium compound. As the organoaluminium compound use is made of compounds having the formula R_nAlX_{3-n}, where X is a halogen atom, an alkoxy group or a hydrogen atom, R is an alkyl group or an aryl group and $1 \leq n \leq 3$. Examples of organoaluminium compounds are trimethyl aluminium, triethyl aluminium, dimethyl aluminium chloride, diethyl aluminium chloride, diethyl aluminium iodide, diisobutyl aluminium chloride, methyl aluminium dichloride, ethyl aluminium dichloride, ethyl aluminium dibromide, isobutyl aluminium dichloride, ethyl aluminium sesquichloride, dimethyl aluminium methoxide, diethyl aluminium phenoxide, dimethylaluminium hydride and diethyl aluminium hydride.

[0045] An external electron donor may also be present during the polymerisation of an olefine. Examples of possible external electron donors are described above with relation to the execution of step c of the preparation of the catalyst component as internal electron donors. As external electron donors also organo-silicon compounds can be used. Mixtures of external electron donors can also be used.

[0046] Examples of organo-silicon compounds that are suitable as external electron donor are: tetramethoxysilane, tetraethoxvsilane, methyltrimethoxysilane, methyltributoxysilane, ethyltriethoxysilane, phenyltriethoxysilane, diethyldiphenoxysilane, diisopropylsilane, diisobutylsilane, n-propyltrimethoxysilane, cyclohexylmethyldimethoxysilane, dicyclopentyldimethoxysilane, isobutyl-isopropyldimethoxylsilane, phenyltrimethoxysilane, diphenyldimethoxysilane, trifluoropropylmethyldimethoxysilane, bis (perhydroisoquinolino) dimethoxysilane, dicyclohexyldimethoxysilane, dinorbornyldimethoxysilane, di (n-propyl) dimethoxysilane and di (n-butyl) dimethoxysilane.

[0047] Preferably an alkoxysilane is used as the external electron donor during the polymerisation.

[0048] The molar ratio of metal in the cocatalyst relative to Ti during the polymerisation may vary from 0.1 to 2000. Preferably this ratio is between 5 and 300. The aluminium/ electron donor molar ratio in the polymerisation mixture is between 0.1 and 200; preferably between 3 and 100.

[0049] The catalyst component is suitable for the polymerisation of mono- and diolefines containing from 2 to 10 carbon atoms, such as ethylene, propylene, butylene, hexene, octene, butadiene and mixtures thereof. The catalyst

component is particularly suitable for the polymerisation of propylene and mixtures of propylene and ethylene.

[0050] The polymerisation can be carried out in the gas phase or in the liquid phase. In the case of polymerisation in the liquid phase a dispersing agent is present, such as n-butane, isobutane, n-pentane, isopentane, hexane, heptane, octane, cyclohexane, benzene, toluene or xylene. Liquid olefine can also be used as a dispersing agent.

[0051] The polymerisation temperature is usually between 0°C and 120°C, preferably it is between 40°C and 100°C.

[0052] The pressure during the polymerisation is normally between 0.1 and 6 MPa. The molecular weight of the polyolefine that is formed during the polymerisation is controlled by adding during the polymerisation hydrogen or any other agent known to be suitable for the purpose.

[0053] The polymerisation can be carried out in continuous mode or batchwise. The polymerisation can be carried out in several, successive steps. The polymerisation can also be carried out by first effecting the polymerisation in the liquid phase and then in the gas phase.

[0054] The invention will be further elucidated with examples without being limited hereto.

Examples

[0055] Abbreviations and measuring methods :

- The weight percentage of atactic polypropylene (APP) was determined as follows: 100 ml of the filtrate (y ml) obtained in separating the polypropylene powder (x g) and the heptane was dried over a steam bath and then under vacuum at 60 °C. That yielded z g of APP. The total amount of APP (q g) is: (y/ 100)*z.
  The weight percentage of APP is: (q/(q+x))*100%.
- The isotacticity index (II) of the polypropylene powder was determined as follows: 5 g of polypropylene powder was extracted with the aid of n-heptane in a Soxhlet extractor for 4 hours. The weight percentage of the polypropylene powder that does not dissolve in n-heptane is the isotacticity index.
- The bulk density (BD) of the polypropylene powder was determined according to ASTM D1895.
- The d_{50} PP and the span of PP powder were determined according to ASTM D1921, method A.
- The d_{50} cat value (µm) was calculated as follows: d_{50} PP*$[1.3\ Y^{1/3}]^{-1}$, werein Y is the number of g of PP powder obtained per g of the catalyst component.

Example I

Preparation of the reaction product I

[0056] A flask, fitted with a reflux condenser and a funnel, was filled with magnesium powder (24.3 g, 1 mol). The flask was brought under nitrogen. The magnesium was heated at 80°C for 1 hour, after which a mixture of dibutyl ether (170 ml) and chlorobenzene (60 ml) was added. Then iodine (0.03 g) and n-chlorobutane (3 ml) were successively added to the reaction mixture. After the colour of the iodine had disappeared, the temperature was raised to 97°C and chlorobenzene (220 ml) was slowly added for 2.5 hours. The dark reaction mixture that was formed in the process was stirred for another 8 hours at 97°C. Then the stirring and heating were stopped and the solid material was allowed to settle for 48 hours. By decanting the solution above the precipitate, a solution of phenylmagnesiumchloride (Ph_xMgCl_{2-x}, reaction product I) with a concentration of 1.36 mol Mg/l has been obtained. This solution was used in the further catalyst preparation.

Preparation of the reaction product II

[0057] The solution of reaction product I (200 ml, 0.272 mol Mg) and 100 ml of the solution of tetraethoxysilane (TES) in dibutyl ether (DBE), (33.4 ml of TES and 66.6 ml of DBE), were cooled to 15°C, and then were dosed simultaneously to a device of 0.45 ml volume supplied with a mixer and jacket. Thereafter the premixed reaction product I and TES-solution were introduced to a reactor. The device with a mixer (minimixer) was cooled to 10°C by means of cold water circulating in the minimixer's jacket. The reagents contact time was 13 s in minimixer and connecting tube between minimixer and reactor. The stirring speed in minimixer was 1000 rpm. The temperature of mixture at the minimixer outlet was 40°C. The mixture formed in minimixer was introduced to a 0.7 1 reactor, with stirring. The reactor was loaded preliminary with 100 ml of DBE, and cooled to 5°C. Dosing time was 1 hour. The stirring speed in reactor was 200 rpm.

[0058] On the dosing completion the reaction mixture was kept at 5°C for 0.5 hour, then heated up to 60°C and kept at this temperature for 1 hour. Then the stirring was stopped and the solid substance was allowed to settle. The supernatant was removed by decanting. The solid substance was washed three times using 300 ml of heptane. As a result, a pale yellow solid substance, reaction product II, was obtained, suspended in 110 ml of heptane.

Preparation of the catalyst

[0059] A reactor was brought under nitrogen and 300 ml of titanium tetrachloride, a slurry, containing 12 g of reaction product II in 36 ml of heptane, and dibutyl phthalate (7.2 ml) were added to it. Then the reaction mixture was kept at 115°C for 2 hours. Then the stirring was stopped and solid substance was allowed to settle. The supernatant was removed by decanting, after which a mixture of titanium tetrachloride (150 ml) and chlorobenzene (150 ml) was added. The reaction mixture was kept at 115°C for 30 min, after which the solid substance was allowed to settle, and the last treatment was repeated once again. The solid substance obtained was washed five times using 300 ml of heptane at 60°C, after which the catalyst component, suspended in heptane, was obtained.

Polymerization of propylene

[0060] Polymerization of propylene was carried out in a stainless steel reactor with a volume of 0.7 l in heptane (300 ml) at a temperature of 70°C, total pressure 0.5 MPa and hydrogen presence (55 ml) for 2 hours. The concentration of catalyst was 0.033 g/l; concentration of triethylaluminium; 4.0 mmol/l; concentration of propyltrimethoxysilane; 0.4 mmol/l. Data on the catalyst performance at propylene polymerization are presented in Table 1. The particles of polymer powder had round shape (Fig. 1).

Example II

[0061]

Preparation of reaction products I and II was carried out as described in Example I, but premixing of solutions of the reaction product I and tetraethoxysilane was carried out in a capillary tube instead of in a minimixer. Premixing time was 4 s.

Preparation of the catalyst and the polymerization of propylene in Example II was carried out as described in Example I. The results are presented in Table 1. The particles of polymer powder had a partially elongated shape.

Comparative Experiment A

[0062]

Reaction product I was prepared as described in Example I.

Preparation of the reaction product II

The solution of reaction product I (200 ml, 0.272 mol Mg) was loaded into a reactor and cooled to 5°C. The mixture of TES (33.4 ml) and DBE (66.6 ml) was dosed into the reactor under stirring for 1 hour. On the dosing completion the preparation of reaction product II was the same as described in Example I.

Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 1. All particles of polymer powder had elongated shape (Fig. 2).

Example III

[0063]

Preparation of the reaction product I

A flask, fitted with a reflux condenser and a funnel, was filled with magnesium powder (24.3 g). The flask was brought under nitrogen. The magnesium was heated at 80°C for 1 hour, after which dibutyl ether (150 ml), iodine (0.03 g) and n-chlorobutane (4 ml) were successively added to a stirred reactor. After the colour of the iodine had disappeared, the temperature was raised to 80°C and a mixture of n-chlorobutane (110 ml) and dibutyl ether (750 ml) was slowly added for 2.5 hours. The reaction mixture was stirred for another 3 hours at 80°C. Then the stirring and heating were stopped and the small amount of solid material was allowed to settle for 24 hours. By decanting the colourless solution above the precipitate, a solution of butylmagnesiumchloride (reaction product I) with a concentration of 1.0 mol Mg/l was obtained.

Preparation of the reaction product II was carried out as described in Example I, but a solution of reaction product I from Example III (200 ml, 0.2 mol Mg) and 100 ml of the solution of tetraethoxysilane (TES) in dibutyl ether (DBE), (17 ml of TES and 83 ml of DBE), were cooled to 10°C, and then were dosed simultaneously to a minimixer of 0.45 ml volume during 100 min. The minimixer was cooled to 10°C by means of cold water circulating in the minimixer's jacket. The reagents contact time was 13 s in minimixer and connecting tube between minimixer and

reactor.
After premixing the mixture was introduced to a 0.7 l reactor, with stirring. The reactor was loaded preliminary with 100 ml of DBE, and cooled to -12°C. On the dosing completion the preparation of reaction product II was the same as described in Example I.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. Data on the catalyst performance are presented in Table 1. The particles of polymer powder had a round shape.

Comparative Experiment B

[0064]

Reaction product I was prepared as described in Example III.
Preparation of the reaction product II
The solution of reaction product I (200 ml, 0.2 mol Mg) was loaded into a reactor and cooled to - 12°C. The mixture of TES (17 ml) and DBE (83 ml) was dosed into a reactor under stirring for 100 min. On the dosing completion the preparation of reaction product II was the same as described in Example I.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. Data on the catalyst performance are presented in Table 1. The particles of polymer powder had a round shape.

Example IV

[0065]

Preparation of the reaction product I
A flask, fitted with a reflux condenser and a funnel, was filled with magnesium powder (19.5 g, 0.8 mol). The flask was brought under nitrogen. The magnesium was heated at 80°C for 1 hour, after which heptane (100 ml), iodine (0.03 g) and n-chlorobutane (3 ml) were successively added to the reactor with the stirring. After the colour of the iodine had disappeared, the temperature was raised to 70°C and mixture of n-chlorobutane (38.5 ml), ethylbromide (30 ml) and 800 ml of heptane was slowly added for 2.5 hours. The reaction mixture was stirred for another 3 hours at 70°C. Then the stirring and heating were stopped and the solid material was allowed to settle for 48 hours. By decanting the colourless solution above the precipitate, a solution of ethylbutylmagnesium (reaction product I) with a concentration of 0.35 mol Mg/l was obtained.
Preparation of the reaction product II
The solution of reaction product I (200 ml, 0.07 mol Mg) and 100 ml of a solution of tetraethoxysilane in heptane, (12.5 ml of TES and 87.5 ml of heptane), were heated to 30°C, and then were dosed simultaneously to a minimixer of 0.45 ml volume. The minimixer was heated to 30°C. The reagents contact time was 22 s in the minimixer and connecting tube between minimixer and reactor. After premixing the mixture was introduced to a 0.7 1 reactor, with stirring. The reactor was loaded preliminary with 100 ml of heptane, and heated to 30°C. Dosing time was 100 min.
On the dosing completion the reaction mixture was kept at 30°C for 0.5 hour, then heated up to 60°C and kept at this temperature for 1 hour. Then the preparation of reaction product II was the same as described in Example I.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. Data on the catalyst performance are presented in Table 1. The particles of polymer powder had a non-regular shape.

Comparative Experiment C

[0066]

Reaction product I was prepared as described in Example IV.
Preparation of the reaction product II
The solution of reaction product I (200 ml, 0.07 mol Mg) was loaded into a reactor and heated to 30°C. The mixture of TES (12.5 ml) and heptane (87.5 ml) was dosed into a reactor under stirring for 100 min. On the dosing completion the preparation of reaction product II was the same as described in Example IV.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. Data on the catalyst performance are presented in Table 1. The particles of polymer powder had a non-regular shape.

Example V

[0067]

Reaction product I was prepared as described in Example 1.

Preparation of the reaction product II

100 ml of dibutyl ether was loaded to 0.7 1 reactor and cooled to 5° C. 200 ml of reaction product I and 100 ml of TES solution (33.4 ml of TES and 66.6 ml of DBE) were dosed simultaneously to a reactor via two separate tubes. Dosing time was 1 hour. On the dosing completion the preparation of reaction product II was the same as described in Example I.

Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. Data on the catalyst performance are presented in Table 2.

Example VI

[0068]

Reaction product I was prepared as described in Example I, but there were used 19.6 g of magnesium powder, 140 ml of dibutyl ether and 310 ml of chlorobenzene. As a result, a solution with a concentration of 1.1 mol Mg/l was obtained.

Preparation of the reaction product II

100 ml of dibutyl ether was loaded to a 0.7 1 reactor and cooled to 10°C. 200 ml of reaction product I and 100 ml of TES solution (27 ml of TES and 73 ml of DBE) were dosed simultaneously to a reactor via two separate tubes. Dosing time was 1 hour. On the dosing completion the preparation of reaction product II was the same as described in Example I.

Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. Data on the catalyst performance are presented in Table 2.

Example VII

[0069]

Reaction product I was prepared as described in Example I.

Reaction product II was prepared as described in Example VI, but the reactor temperature on dosing was 20°C.

Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are given in Table 2.

Example VIII

[0070]

Reaction product I was prepared as described in Example I.

Reaction product II was prepared as described in Example VI, but the dosing temperature in reactor was 30°C.

Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are given in Table 2.

Example IX

[0071]

Reaction product I was prepared as described in Example I.

Preparation of the reaction product II was carried out as described in Example I, but before premixing the solutions of the reaction product I and tetraethoxysilane were cooled to -15°C, and as a result the temperature of the mixture at the minimixer outlet was 16°C.

Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 3.

Example X

[0072]

Reaction product I was prepared as described in Example I.
Preparation of the reaction product II was carried out as described in Example I, but before premixing the solutions of the reaction product I and tetraethoxysilane were heated to 55°C, and as a result the temperature of the mixture at the minimixer outlet was 66°C.
Preparation of the catalyst and the polymerization of propylene was carried out as described in Example I. The final results are presented in Table 3.

Example XI

[0073]

Reaction product I was prepared as described in Example I.
Preparation of the reaction product II was carried out as described in Example I, but the volume of solutions of the reaction product I and tetraethoxysilane was two times larger than that in Example 1, and as a result the premixing time was two times less: 6.5 s.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 3.

Example XII

[0074]

Reaction product I was prepared as described in Example I.
Preparation of the reaction product II was carried out as described in Example I, but the total volume of the minimixer and tube between minimixer and reactor was two times larger than that in Example I, and as a result the premixing time was two times longer: 26 s.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 3.

Example XIII

[0075]

Reaction product I was prepared as described in Example I.
Preparation of the reaction product II was carried out as described in Example XII, but solutions of the reaction product I and tetraethoxysilane were cooled to -15°C, as in Example IX, and as a result a temperature of mixture at the minimixer outlet was 16°C.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 3.

Example XIV

[0076]

Reaction product I was prepared as described in Example I, but a solution with a concentration of 1.3 mol Mg/l was obtained.
Preparation of the reaction product II was as described in Example I, but the reactor was cooled to 0°C.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 4.

Example XV

[0077]

Reaction product I was prepared as described in Example I.
Preparation of the reaction product II was as described in Example XIV, but the premixing time was 6.5 s, and the dosing time was 30 min.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 4.

Example XVI

[0078]

Preparation of reaction product I was carried out as described in Example I, but the quantity of a reagents was: magnesium - 360 g; dibutyl ether - 2.6 l; chlorobenzene - 4.6 1; n-chlorobutane - 50 ml; iodine - 0.5 g. Preparation was carried out in stainless steel reactor of 9 1 volume. As a result, the solution (ca. 4 1) of reaction product I with a concentration of 1.3 mol Mg/l was prepared.
Preparation of the reaction product II was carried out as described in Example I, but the quantity of a reagents was 10 times larger, premixing of reagents was carried out in minimixer of 4 ml volume and the volume of stainless steel reactor was equal 5 1. The dosing time was 120 min. The stirring speed in minimixer and reactor was 600 and 150 rpm, correspondingly.
Preparation of catalyst was carried out as described in Example I, but the quantity of reagents was 20 times larger and preparation was carried out in stainless steel reactor of the 9 1 volume. The final results are presented in Table 4.

Example XVII

[0079]

Preparation of reaction product I was carried out as described in Example I, but the quantity of a reagents was the next: magnesium - 292 g; dibutyl ether - 2 l; chlorobenzene - 4.6 1; As a result, 4 1 of solution of reaction product I with a concentration of 1 mol Mg/l was prepared.
Preparation of reaction product II was carried out as described in Example I, but a volume of minimixer was 0.15 ml, premixing time was 19 s, dosing time was 120 min and volume of DBE in reactor was 250 ml.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 4.

Example XVIII

[0080]

Preparation of the reaction product I was carried out as described in Example XVII.
Preparation of the reaction product II was carried out in stainless steel reactor of the 5 1 volume, the volume of minimixer was 1.4 ml, the quantity of reagents was 8 times larger, than that in Example XVII, premixing time was 19 s and dosing time was 240 min.
Preparation of catalyst was carried out as described in Example I, but the quantity of reagents was 20 times larger and preparation was carried out in stainless steel reactor of the 9 1 volume.
The polymerization of propylene was carried out as described in Example I. The final results are presented in Table 4.

Example XIX

[0081]

Preparation of the reaction product I was carried out as described in Example I, but the quantity of magnesium was 380 g. As a result, 3.6 1 of solution of reaction product I with a concentration of 1.4 mol Mg/l was prepared.
Preparation of the reaction product II was carried out as described in Example I, but the quantity of a reagents

was 10 times larger, premixing of reagents was carried out in minimixer of the 4 ml volume and the volume of stainless steel reactor was equal to 5 l. Premixing time was 7.2 sec, dosing time was 70 min, the temperature in reactor was 10°C and stirring speed in reactor was 125 rpm.
Preparation of catalyst was carried out as described in Example I, but the quantity of reagents was 20 times larger and preparation was carried out in stainless steel reactor of the 9 1 volume.
The polymerization of propylene was carried out as described in Example I. The final results are presented in Table 4.

Example XX

[0082]

Preparation of the reaction product I was carried out as described in Example XVI.
Preparation of the reaction product II

130 ml of dibutyl ether was introduced to a reactor. The reactor was thermostated at 20°C. Then the solution of reaction product I (400 ml, 0.52 mol Mg) and solution of tetraethoxysilane (64 ml) in dibutyl ether (136 ml) was dosed into reactor for 400 min with preliminary mixing in minimixer of 0.15 ml volume. Solution of reaction product I and TES solution was preliminary cooled as in Example I. Premixing time was 18 s. On the dosing completion the preparation of reaction product II was the same as described in Example I.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 4.

Example XXI

[0083]

Reaction product I was prepared as described in Example I.
Preparation of the reaction product II was as described in Example XX, but the dosing temperature of the reactor was 30°C.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 4.

Example XXII

[0084]

Reaction product I was prepared as described in Example I.
Preparation of the reaction product II was as described in Example XXI, but the quantity of reagents was 2.5 times larger and the dosing time was 18 hours.
Preparation of the catalyst and the polymerization of propylene were carried out as described in Example I. The final results are presented in Table 4.

[0085] The invention is directed to the production of a catalyst compound and/or polymer particles with an improved morphology over the catalysts and/or polymer particles described in WO-A-96/32427.

[0086] When comparing Examples 1 and 2 with Comparative Experiment A the improved morphology is illustrated by the round particles and the higher bulk density.
When comparing Example 3 with Comparative Experiment B the improved morphology is illustrated by a narrow particle size distribution and a higher bulk density. When comparing Example 4 with Comparative Experiment C the improved morphology is illustrated by a higher bulk density.

Table 1.

Ex. No.	reaction product II		Ti, wt.%	Yield, kg PP/ g cat	APP, wt.%	I.I., wt.%	BD, g/l	D_{50}PP, µm	SPAN	d_{50}cat. µm
	type	[Mg] mol/l								
I	Ph_xMgCl_{2-x}	1.36	2.6	7.1	1.1	98.0	380	890	0.44	32.0
II	Ph_xMgCl_{2-x}	1.36	2.6	8.7	0.9	97.2	350	1260	0.63	47.0
A	Ph_xMgCl_{2-x}	1.36	2.9	5.0	1.2	97.5	280	700	0.63	31.5
III	BuMgCl	1.0	2.6	5.2	1.0	97.6	430	370	0.4	16.0
B	BuMgCl	1.0	2.2	4.3	0.5	98.5	410	430	1.1	20.0
IV	EtMgBu	0.35	3.8	9.8	1.2	97.2	310	1400	2.0	50.5
C	EtMgBu	0.35	5.3	6.6	1.4	97.0	270	1420	2.0	58.5

Table 2.

Ex. No.	Dosing temperature, °C	Ti, wt.%	Yield, kg PP/g cat	APP, wt.%	I.I. wt.%	BD, g/l	D_{50}PP, µm	SPAN	d_{50}cat., µm
V	5	2.3	8.8	0.8	98.2	360	930	0.61	35
VI	10	1.7	7.0	0.8	98.2	400	720	0.89	29
VII	20	2.4	6.9	0.8	97.9	370	710	0.5	28
VIII	30	2.6	7.4	0.7	98.0	330	900	0.9	36

Table 3.

Ex. No.	Temperature of mixture (at the minimixer outlet), ^{o}C	Premixing time, sec	Ti, wt. %	Yield, kg PP/g cat	APP, wt.%	I.I. wt.%	BD, g/l	D_{50}PP, µm	SPAN	d_{50}cat., µm
IX	16	13	3.2	6.7	0.8	97.4	375	850	0.51	35
X	66	13	3.1	7.8	1.1	97.4	385	420	0.95	16
XI	40	6.5	2.8	6.4	1.0	96.8	330	1170	0.72	48
XII	40	26	2.2	6.8	1.0	96.4	370	580	0.41	24
XIII	16	26	2.4	7.9	0.9	96.5	400	940	0.31	36

Table 4.

Ex. No.	Dosing temperature in reactor, °C	Dosing time, min	Ti, wt.%	Yield, kg PP/g cat	APP, wt.%	I.I. wt.%	BD, g/l	D_{50}PP, µm	SPAN	d_{50}cat., µm
XIV	0	60	2.2	8.0	0.8	97.9	400	890	0.25	34
XV	0	30	2.4	6.8	1.2	97.5	390	1030	0.95	42
XVI	5	120	2.1	8.4	0.6	98.3	415	870	0.31	33
XVII	5	120	2.7	9.4	0.8	98.0	405	520	0.21	19
XVIII	5	240	2.5	11.5	0.5	98.5	430	440	0.41	15
XIX	10	70	2.4	10.0	0.5	98.3	340	1900	0.66	70
XX	20	400	2.8	7.4	0.7	97.8	425	1040	0.31	45
XXI	30	400	2.9	7.0	0.6	98.0	435	1000	0.40	39
XXII	30	1080	2.6	7.2	0.6	98.2	450	770	0.64	31

Claims

1. Process for the preparation of a catalyst component for the polymerisation of an olefin by:

   a) contacting metallic magnesium with an organic halide RX, where R is an organic group containing from 1 to 20 carbon atoms and X is a halide, whereupon the dissolved reaction product I is separated from the solid residual products and whereafter,
   b) an alkoxy group or aryloxy group-containing silane compound is added to the obtained reaction product I, whereupon the precipitate formed is purified to obtain reaction product II,
   c) which subsequently is contacted with $TiCl_4$ as halogenized titanium compound and is purified to obtain a catalyst component,

   characterized in that,
   in step b the silane compound and reaction product I are introduced simultaneously to a device.

2. Process according to claim 1, characterized in that, the device is a device suitable for the premixing of the silane compound and reaction produkt I before introduction of the mixture in the reactor wherein reaction product II is collected.

3. Process according to claim 2, characterized in that, the device is a static mixer.

4. Process according to any one of claims 2-3, characterized in that, premixing is performed during 0.1 to 300 seconds.

5. Process according to any one of claims 2-3, characterized in that, premixing is performed during 1 to 50 seconds.

6. Process according to anyone of claims 2-5, characterized in that, the temperature during premixing is 0 to 80 °C.

7. Process according to anyone of claims 2-5, characterized in that, the temperature during premixing is 10 to 50 °C.

8. Process according to claim 1, characterized in that, the device is a reactor wherein reaction product II is formed.

9. Process according to anyone of claims 1-8, characterized in that an internal donor compound is introduced during step c.

10. Process for the polymerisation of olefin monomers using a catalyst component and a cocatalyst, characterized in that, a catalyst component obtainable by the process according to claims 1-9 is used.

11. Process according to claim 10, characterized in that, propylene or a mixture op propylene and ethylene is polymerised.

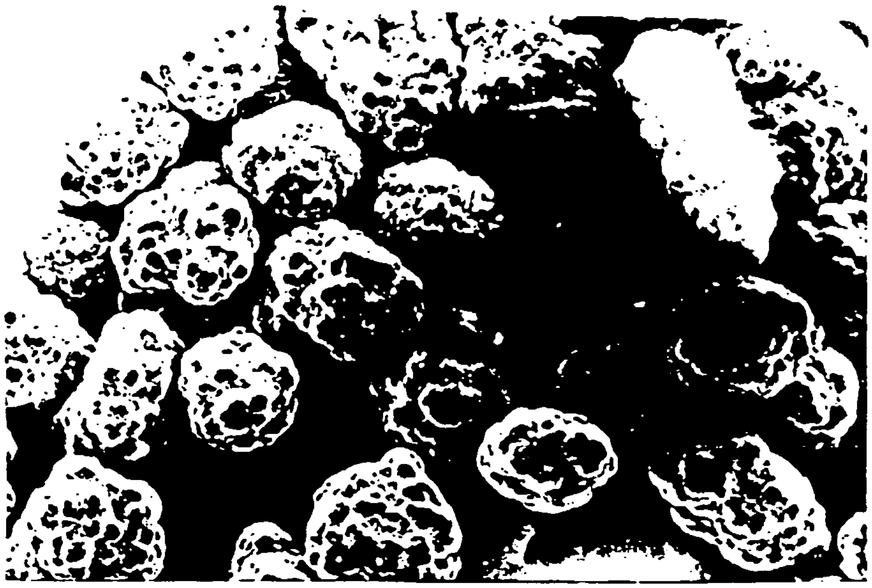

FiG. 1

FiG. 2

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EUROPEAN SEARCH REPORT

Application Number
EP 99 20 3144

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The present search report has been drawn up for all claims

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MUNICH	9 March 2000	Van Golde, L

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